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(54) Title: NAPHTHALENEDICARBOXYLATE CONTAINING POLYESTER/POLYAMIDE BLEND HAVING IMPROVED FLAVOR RETAINING PROPERTY			
(57) Abstract The present invention comprises polyester blend compositions having improved flavor retaining properties and color, comprising: (A) 98.0 to 99.95 weight percent of a polyester which comprises (1) a dicarboxylic acid component comprising repeat units from at least 50 mole percent naphthalenedicarboxylic acid; and (2) a diol component comprising repeat units from at least 50 mole percent ethylene glycol, based on 100 mole percent dicarboxylic acid and 100 mole percent diol; and (B) 2.0 to 0.05 weight percent of a polyamide; wherein the combined weights of (A) and (B) total 100 percent.			

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**NAPHTHALENEDICARBOXYLATE CONTAINING
POLYESTER/POLYAMIDE BLEND HAVING IMPROVED FLAVOR
RETAINING PROPERTY**

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RELATED APPLICATIONS

This application claims priority of provisional application Serial No. 60\036,008 filed March 5, 1997.

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FIELD OF THE INVENTION

The container market for carbonated and still mineral water requires exceptionally low levels of acetaldehyde (AA) in the container side wall in order to avoid the diffusion of the AA into the water leading to an undesirable water taste. AA is an inherent side product which is generated during the polymerization melt phase and subsequent processing steps. In addition, variables such as catalyst selection influence the amount of residual AA. Despite the significant improvement in the PET presently produced, this level of AA is still perceived to be too high for some applications. In fact, taste testing has indicated that humans can taste 20 ppb differences in AA. Consequently, there has been significant interest in reducing the residual AA content as low as possible.

In addition to very low levels of residual AA in the bottle sidewall, the market also demands that the product color be as low as possible. The lack of significant bottle sidewall color permits the use of "natural" or colorless water bottles, and also facilitates the intentional addition of dyes to generate a desired color bottle. Bottle sidewall color is typically reported as a b* unit which reflects the level of yellow color in the bottle. For example, containers prepared from virgin PET resin have values ranging from 0.8-1.2 b* units. Consequently, significant attention has been devoted to the production of beverage containers which demonstrate both low AA and low color.

US patents 5,258,233, 5,266,413, 5,340,884 disclose polyamide/PET homopolymer blends, PET/polyamide copolymers, and PET/polyamide based concentrates. However, the end products have AA and/or color levels which are still undesirable for certain applications.

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The use of various polyamides to increase the gas barrier properties in polyethylene terephthalate resins is disclosed in U.S. Pat. Nos. 4,837,115, 4,052,481 and 4,501,781.

U.S. Pat. No. 4,837,115 discloses a thermoplastic composition containing
5 polyethylene terephthalate and high molecular weight polyamides which act to reduce the residual acetaldehyde contained in the polyester. U.S. Pat No. 4,837,115 states that the molecular weight of the polyamide is not critical so far as the polyamide has a film-forming property. Such polyamides, therefore, must have high enough molecular weights to form a film. It is well known in the art that polyamides
10 having molecular weights of at least 12,000 are necessary to form a film.

DESCRIPTION OF THE INVENTION

The present invention comprises semi-crystalline polyester blend compositions having improved flavor retaining properties, comprising:

- 15 (A) 98.0 to 99.95 weight percent of a polyester which comprises
(1) a dicarboxylic acid component comprising repeat units from at least 50 mole percent naphthalenedicarboxylic acid derived from at least one dimethylester of naphthalenedicarboxylic acid respectively; and
(2) a diol component comprising repeat units from at least 50 mole percent
20 ethylene glycol, based on 100 mole percent dicarboxylic acid and 100 mole percent diol; and

(B) 2.0 to 0.05 weight percent of a polyamide;
wherein the combined weights of (A) and (B) total 100 percent.

The present invention further comprises a process for forming a polymer/polyamide
25 blend comprising blending

- (A) about 80 to about 99 weight % of a base polyester comprising
(1) a dicarboxylic acid component comprising repeat units from at least
about 85 mole percent naphthalenedicarboxylic acid thereof, wherein
said acid is derived from terephthalic acid or naphthalenedicarboxylic
30 acid respectively; and

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- (2) a diol component comprising repeat units from at least about 85 mole percent ethylene glycol, based on 100 mole percent dicarboxylic acid and 100 mole percent diol; and
- B) about 1 to about 20 weight % of a concentrate comprising:
- 5 1) about 1 to about 99 weight % of a carrier resin comprising repeat units from at least about 60 mole percent naphthalenedicarboxylic acid and mixtures thereof, and a diol component comprising repeat units from at least about 50 mole percent ethylene glycol, based on 100 mole percent dicarboxylic acid and 100 mole percent diol; and
- 10 (2) about 1 to about 99 weight% of a polyamide which displays a melting point below the melting point of said carrier resin.

Thus the present invention involves naphthalenedicarboxylate polyester/polyamide blends having surprisingly low AA. The present invention further discloses naphthalenedicarboxylate containing polyester/polyamide blends which are formed by mixing a polyester base resin with a concentrate containing the

15 polyamide.

The polyester (A), of the present invention is selected from polyethylene naphthalenedicarboxylate (PEN) or copolyesters thereof. The acid component of polyester (A) contains repeat units from at least about 50 mole percent

20 naphthalenedicarboxylic acid and at least about 50 mole percent ethylene glycol, based on 100 mole percent dicarboxylic acid and 100 mole percent diol.

It should be understood that use of the corresponding acid, ester and acid anhydrides and acid chlorides of the acids may be used to supply the acid component. Preferably the naphthalenedicarboxylate repeat unit is supplied from the

25 diester.

The dicarboxylic acid component of the polyester may optionally be modified with up to about 50 mole percent and more preferably 15 mol% of one or more different dicarboxylic acids. Such additional dicarboxylic acids include aromatic dicarboxylic acids preferably having 8 to 14 carbon atoms, aliphatic

30 dicarboxylic acids preferably having 4 to 12 carbon atoms, or cycloaliphatic

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dicarboxylic acids preferably having 8 to 12 carbon atoms. Examples of dicarboxylic acids include: terephthalic acid, phthalic acid, isophthalic acid, cyclohexanedicarboxylic acid, cyclohexanediacetic acid, diphenyl-4,4'-dicarboxylic acid, succinic acid, glutaric acid, adipic acid, azelaic acid, sebacic acid, and the like.

5 Polyesters may be prepared from two or more of the above dicarboxylic acids.

In addition, the glycol component (A)(2), may optionally be modified with up to about 50 mole percent and more preferably up to about 15 mole percent, of one or more different diols other than ethylene glycol. Such additional diols include cycloaliphatic diols preferably having 6 to 20 carbon atoms or aliphatic diols preferably having 3 to 20 carbon atoms. Examples of such diols to be included with ethylene glycol are: diethylene glycol, triethylene glycol, 1,4-cyclohexanedimethanol, propane-1,3-diol, butane-1,4-diol, pentane-1,5-diol, hexane-1,6-diol, 3-methylpentanediol-(2,4), 2-methylpentanediol-(1,4), 2,2,4-trimethylpentane-diol-(1,3), 2-ethylhexanediol-(1,3), 2,2-diethylpropane-diol-(1,3), hexanediol-(1,3), 1,4-di-(hydroxyethoxy)-benzene, 2,2-bis-(4-hydroxycyclohexyl)-propane, 2,4-dihydroxy-1,1,3,3-tetramethyl-cyclobutane, 2,2-bis-(3-hydroxyethoxyphenyl)-propane, and 2,2-bis-(4-hydroxypropoxyphenyl)-propane. Polyesters may be prepared from two or more of the above diols.

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The resin may also contain small amounts of trifunctional or tetrafunctional comonomers such as trimellitic anhydride, trimethylolpropane, pyromellitic dianhydride, pentaerythritol, and other polyester forming polyacids or polyols generally known in the art. Preferably the carrier and base resins of the present invention should have molecular weights which are sufficient to insure that bottles may be formed from the resin. More preferably the resins have I.V. which are between about 0.60 and about 1.3 dl/gm, as determined in a 70:30 phenol:trichloroethane cosolvent.

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The PEN based polyesters of the present invention can be prepared by conventional polycondensation procedures well-known in the art. Such processes include direct condensation of the dicarboxylic acid(s) or diester(s) with the diol(s). The polyesters may also be subjected to solid state polymerization methods.

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The second component of the present invention is a polyamide capable of decreasing the AA which is generated during the production of the base resin and subsequent processing steps. Suitable polyamides display a melting point below the melting point of the polyester (PEN homopolymer, copolymer or blends).

- 5 Preferably said polyamide is selected from the group consisting of low molecular weight partially aromatic polyamides having a number average molecular weight of less than 15,000, low molecular weight aliphatic polyamides having a number average molecular weight of less than 7,000 and wholly aromatic polyamides.

Combinations of such polyamides are also included within the scope of the
10 invention. By "partially aromatic polyamide" it is meant that the amide linkage of the partially aromatic polyamide contains at least one aromatic ring and a nonaromatic species.

The partially aromatic polyamides have an I.V. of less than about 0.8 dL/g. Preferably the I.V. of the partially aromatic polyamides is less than about 0.7 dL/g
15 and the number average molecular weight is less than about 12,000.

The aliphatic polyamides have an I.V. of less than about 1.1 dL/g. Preferably the I.V. of the aliphatic polyamides is less than about 0.8 dL/g and the number average molecular weight is less than about 6,000. Wholly aromatic polyamides comprise in the molecule chain at least 70 mole % of structural units
20 derived from m-xylylene diamine or a xylylene diamine mixture comprising m-xylylene diamine and up to 30% of p-xylylene diamine and an α -aliphatic dicarboxylic acid having 6 to 10 carbon atoms, which are further described in Japanese Patent Publications No. 1156/75, No. 5751/75, No. 5735/75 and No. 10196/75 and Japanese Patent Application Laid Open Specification No. 29697/75.

25 The composition or articles of the present invention may contain up to about two weight percent of the low molecular weight polyamides and preferably less than about one weight percent. It has been determined that the use of polyamides at greater than about two weight percent based on the weight of the polyester cause undesirable levels of haze.

30 Low molecular weight polyamides formed from isophthalic acid, terephthalic

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acid, cyclohexanedicarboxylic acid, 2,6- and/or 1,5 naphthalenedicarboxylic acid, adipic acid, *meta*- or *para*-xylylene diamine, 1,3- or 1,4-cyclohexane(bis)methylamine, aliphatic diacids with 6 to 12 carbon atoms, aliphatic amino acids or lactams with 6 to 12 carbon atoms, aliphatic diamines with 4 to 12 carbon atoms, and other generally known polyamide forming diacids and diamines. Preferably polyamides used in the present invention are derived from 2,6-naphthalenedicarboxylic acid either alone or in combination with other acids such as adipic acid. The low molecular weight polyamides may also contain small amounts of trifunctional or tetrafunctional comonomers such as trimellitic anhydride, pyromellitic dianhydride, or other polyamide forming polyacids and polyamines known in the art.

Preferred low molecular weight partially aromatic polyamides include: poly(*m*-xylylene adipamide), poly(hexamethylene isophthalamide), poly(hexamethylene adipamide-co-isophthalamide), poly(hexamethylene adipamide-co-terephthalamide), and poly(hexamethylene isophthalamide-co-terephthalamide).

The most preferred low molecular weight partially aromatic polyamide is poly(*m*-xylylene adipamide) having a number average molecular weight of about 4,000 to about 7,000 and an inherent viscosity of about 0.3 to about 0.6 dL/g.

Preferred low molecular weight aliphatic polyamides include poly(hexamethylene adipamide) and poly(caprolactam). The most preferred low molecular weight aliphatic polyamide is poly(hexamethylene adipamide) having a number average molecular weight of about 3,000 to about 6,000 and an inherent viscosity of 0.4 to 0.9 dL/g. Low molecular weight partially aromatic polyamides, are preferred over the aliphatic polyamides where clarity and dispersibility are crucial.

Preferred low molecular weight aliphatic polyamides include polycapramide (nylon 6), poly- ω -aminoheptanoic acid (nylon 7), poly- ω -aminonanoic acid (nylon 9), polyundecane-amide (nylon 11), polyaurylactam (nylon 12), polyethylene-adipamide (nylon 2,6), polytetramethylene-adipamide (nylon 4,6), polyhexamethylene-adipamide (nylon 6,6), polyhexamethylene-sebacamide (nylon

6,10), polyhexamethylene-dodecamide (nylon 6,12), polyoctamethylene-adipamide (nylon 8,6), polydecamethylene-adipamide (nylon 10,6), polydodecamethylene-adipamide (nylon 12,6) and polydodecamethylene-sebacamide (nylon 12,8).

5 The low molecular weight polyamides are generally prepared by melt phase polymerization from a diacid-diamine complex which may be prepared either in situ or in a separate step. In either method, the diacid and diamine are used as starting materials. Alternatively, an ester form of the diacid may be used, preferably the dimethyl ester. If the ester is used, the reaction must be carried out at a relatively low temperature, generally 80 to 120°C., until the ester is converted to an amide.

10 The mixture is then heated to the polymerization temperature. In the case of polycaprolactam, either caprolactam or 6-aminocaproic acid can be used as a starting material and the polymerization may be catalyzed by the addition of adipic acid/hexamethylene diamine salt which results in a nylon 6/66 copolymer. When the diacid-diamine complex is used, the mixture is heated to melting and stirred until

15 equilibration.

 The molecular weight is controlled by the diacid-diamine ratio. An excess of diamine produces a higher concentration of terminal amino groups. Conversely, an excess of the diacid leads to a higher concentration of terminal acid groups. If the diacid-diamine complex is prepared in a separate step, excess diamine is added prior

20 to the polymerization. The polymerization can be carried out either at atmospheric pressure or at elevated pressures.

 The process for preparing the polyester/polyamide blends of the present invention involve preparing the polyester and low molecular weight polyamide, respectively, by processes as mentioned previously. The polyester and polyamide

25 are dried in an atmosphere of dried air or dried nitrogen, or under reduced pressure.

 The polyester and polyamide are mixed and subsequently melt compounded, for example, in a single or twin screw extruder. Melt temperatures must be at least as high as the melting point of the polyester and are typically in the range of about 260 to about 310°C. Preferably, the melt compounding temperature is maintained as

30 low as possible within said range. After completion of the melt compounding, the

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extrudate is withdrawn in strand form, and recovered according to the usual way such as cutting. Instead of melt compounding, the polyester and polyamide may be dry-blended and heat-molded or draw-formed into plastic articles.

5 The polyamide can be added in the late stages of polyester manufacture. For example, the polyamide can be blended with the molten polyester as it is removed from the polycondensation reactor, before it is pelletized. This method, however, is not desirable if the polyester/polyamide blend will be subjected to solid state polymerization since undesirable color and/or haze may develop during extended time at elevated temperatures.

10 The polyamide may also be added as part of a polyolefin based nucleator concentrate where clarity is not critical such as in crystallized thermoformed articles. The polyamide may also be as a component of a polyester concentrate. The concentrate carrier resin may use either the acid or ester form of the acid component of the polyester. Preferably the carrier resin is derived from the acid form.

15 Generally the concentrate comprises about 1 to about 99 weight % of a carrier resin comprising repeat units from at least about 60 mole percent naphthalenedicarboxylic acid and a diol component comprising repeat units from at least about 50 mole percent ethylene glycol, based on 100 mole percent dicarboxylic acid and 100 mole percent diol and about 1 to about 99 weight% of a polyamide
20 described above. More preferably the carrier resin is about 20 to about 99 and most preferably about 50 to about 99 weight percent.

 Generally between about 1 and about 20 weight percent of the concentrate is added to the base resin. More preferably about 1 to about 10 weight percent of the concentrate is added.

25 The blends of this invention serve as excellent starting materials for the production of moldings of all types by extrusion or injection molding. Specific applications include various packaging applications such as thermoformed or injection molded trays, lids and cups; injection stretch blow-molded bottles, film and sheet; extrusion blow-molded bottles and multilayer articles. Examples of package
30 contents include, but are not limited to, food, beverages, and cosmetics.

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Many other ingredients can be added to the compositions of the present invention to enhance the performance properties of the blends. For example, crystallization aids, impact modifiers, surface lubricants, denesting agents, stabilizers, antioxidants, ultraviolet light absorbing agents, metal deactivators, colorants such as, but not limited to titanium dioxide and carbon black, nucleating agents such as polyethylene and polypropylene, phosphate stabilizers, fillers, and the like, can be included herein. All of these additives and the use thereof are well known in the art and do not require extensive discussions. Therefore, only a limited number will be referred to, it being understood that any of these compounds can be used so long as they do not hinder the present invention from accomplishing its objectives.

Suitable colorants can be added to either component of the blend during polymerization or added directly to the blend during compounding. If added during blending, the colorant can be added either in pure form or as a concentrate. The amount of a colorant depends on its absorptivity and the desired color for the particular application. A preferred colorant is 1-cyano-6-(4-(2-hydroxyethyl)anilino)-3-methyl-3H-dibenzo(F,I,J)-isoquinoline-2,7-dione used in an amount of from about 2 to about 15 ppm.

Desirable additives also include impact modifiers and antioxidants. Examples of typical commercially available impact modifiers well-known in the art and useful in this invention include ethylene/propylene terpolymers, styrene based block copolymers, and various acrylic core/shell type impact modifiers. The impact modifiers may be used in conventional amounts from about 0.1 to about 25 weight percent of the overall composition and preferably in amounts from about 0.1 to about 10 weight percent of the composition. Examples of typical commercially available antioxidants useful in this invention include, but are not limited to, hindered phenols, phosphites, diphosphites, polyphosphites, and mixtures thereof. Combinations of aromatic and aliphatic phosphite compounds may also be included.

Acetaldehyde generation (AA Gen) was determined by the following method. After crystallizing for 30 minutes at 180°C., the pelletized polyester was

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dried overnight at 120°C. in a vacuum oven. A Tinius-Olsen melt indexer was loaded with 5 grams of the polyester and held at the test temperature for five minutes. The molten polyester was extruded into water and stored at a temperature of -40°C. until grinding. The sample was ground to 20 mesh or finer and 0.5 grams
5 was placed in a sample tube which was immediately sealed. The sample was analyzed by dynamic headspace gas chromatographic analysis using a Hewlett-Packard 5890 Gas Chromatograph with a Perkin Elmer Automatic Thermal Desorption ATD-50 as the injection system. Acetaldehyde was desorbed by heating the sample at 150°C. for ten minutes. The gas chromatography column had a 30 m
10 by 0.53 mm inside diameter.

Acetaldehyde concentration after extrusion (Extrusion AA) was determined by grinding the pellets or sheet to 20 mesh or finer and measuring the acetaldehyde concentration by the same gas chromatographic method as described for acetaldehyde generation.

15 Color was determined according to ASTM D2244 using a Hunter Color Lab instrument. Color measurements are reported as Rd, a and b.

Haze was determined by ASTM D1003. Haze values of greater than 3.0% indicate visible haze.

Inherent viscosity (I.V.) was measured at 25°C using 0.50 grams of polymer
20 per 100 ml of a solvent consisting of 60% by weight phenol and 40% by weight tetrachloroethane.

EXAMPLE 1

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Poly(*m*-xylylene adipamide) was prepared by the following procedure.

A mixture containing 4.32 kg of adipic acid, 4.82 kg of *m*-xylylenediamine and 7.72 kg of water, was prepared. The mixture was placed in a polymerization reactor under a nitrogen atmosphere. The mixture was heated with stirring to reflux for 30 minutes. The mixture was heated to 120°C. and held for 60 minutes while water was distilled off. The temperature was then increased to 275°C. over a period of 3.25 hours. The mixture was stirred at 275°C. for 30 minutes. The poly(*m*-xylylene adipamide) was extruded into water, ground and dried. The number average molecular weight and I.V. of the poly(*m*-xylylene adipamide) was determined to be 2,300 and 0.27 dL/g, respectively.

Poly(*m*-xylylene adipamide) prepared according to the above procedure was used to prepare a concentrate containing 25 weight percent of the polyamide in POLYESTER A. The polyamide was pulverized and subsequently dried at 120°C. for 16 hours in a vacuum oven.

EXAMPLE 2-4

PEN containing the low AA concentrate was prepared as follows:

Three samples of PEN homopolymer having an I.V. of 0.56 dL/g were modified with an amount of concentrate sufficient to deliver the amount of polyamide listed in Table 1 below. The low AA concentrate prepared in Example 1 was added just prior to extrusion to form polymer pellets at 295°C and the resulting polymer was molded into pellets. The AA concentration after extruding was measured and compared to the control reported in Table 2 to determine the % AA reduction as and is shown in Table 1, below.

TABLE 1

Example #	% PA in PEN	% AA Reduction
2	0.5	21
3	1	43
4	2	64

- Thus, the results in Table 1 clearly show that additions of even small amounts of AA reducing concentrates substantially reduces the amount of AA in PEN polymers.

5

Examples 5-10

- The effect of the concentrates in PEN (homopolymer and a copolymer of 92 mole% N, 8 mole%T and 100 mole %EG) was compared against the effect of the concentrate in PET. Examples 5-7 report the amount of AA present in the unmodified base polymers. Examples 8-10 were prepared as above, except that the amount of polyamide delivered was kept constant (0.5 wt%) and the carrier resin (or concentrate) resin used was the same as the base polymer. Table 2 shows the amount of AA in the extruded pellets and the corresponding %AA reduction compared to the controls (Examples 5-7).

10

TABLE 2

Ex.#	Base Polymer	Conc. Resin	AA ppm	% AA redxn
5	PET	-	6.47	na
6	PENT	-	109	na
7	PEN	-	66.3	na
8	PET	PET	0.92	86
9	PENT	PENT	40.4	63
10	PEN	PEN	18.7	72

PENT = 92 mole% N, 8 mole%T and 100 mole %EG

PEN is generally processed at temperatures which are 10-20° greater than those for PET due to PEN's higher melting temperature. Unfortunately the amount of AA generated in a polymer derived or containing ethylene glycol nearly exponentially increases as the processing temperature is increased. For example, the amount of AA generated in PET at 295°C (approximately the processing temperature for PEN) is nearly double the amount generated at 275°C. Thus, it was very surprising that the AA reducing agents of the present invention could still produce significant reductions in AA in PENT and PEN polymers despite their higher required processing temperatures and corresponding higher rates of AA generation.

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WHAT IS CLAIMED IS:

1. Polyester compositions having improved flavor retaining properties, comprising:

5 (A) about 98.0 to about 99.95 weight percent of a polyester which comprises

(1) a dicarboxylic acid component comprising repeat units from at least about 50 mole percent naphthalenedicarboxylic acid; and

10 (2) a diol component comprising repeat units from at least about 50 mole percent ethylene glycol, based on 100 mole percent dicarboxylic acid and 100 mole percent diol; and

(B) about 2.0 to about 0.05 weight percent of a polyamide;

wherein the combined weight percents of (A) and (B) total 100 percent.

2. The composition of claim 1 wherein said polyamide is selected from the group consisting of low molecular weight partially aromatic polyamides having a
15 number average molecular weight of less than 15,000, low molecular weight aliphatic polyamides having a number average molecular weight of less than 7,000 and wholly aromatic polyamides.

3. The composition of claim 1 wherein the polyamide comprises a fully aliphatic polyamide selected from the group consisting of polycapramide (nylon 6),
20 poly- ω -aminoheptanoic acid (nylon 7), poly- ω -aminonanoic acid (nylon 9), polyundecane-amide (nylon 11), polyaurylactam (nylon 12), polyethylene-adipamide (nylon 2,6), polytetramethylene-adipamide (nylon 4,6), polyhexamethylene-adipamide (nylon 6,6), polyhexamethylene-sebacamide (nylon 6,10),
25 polyhexamethylene-dodecamide (nylon 6,12), polyoctamethylene-adipamide (nylon 8,6), polydecamethylene-adipamide (nylon 10,6), polydodecamethylene-adipamide (nylon 12,6) and polydodecamethylene-sebacamide (nylon 12,8).

4. The compositions of claim 2 wherein said partially aromatic polyamides have an I.V. of less than about 0.8 dL/g.

5. The compositions of claim 2 wherein said polyamide contains at least one
30 partially aromatic polyamide having an I.V. of less than about 0.7 dL/g and a

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number average molecular weight of less than about 12,000.

6. The composition of claim 2 wherein said polyamide contains at least one aliphatic polyamide having an I.V. of less than about 1.1 dL/g.

7. The composition of claim 6 wherein said at least one aliphatic polyamide
5 has an I.V. of less than about 0.8 dL/g and said number average molecular weight is less than about 6,000.

8. The compositions of claim 1 wherein said polyamide further comprises small amounts of trifunctional or tetrafunctional comonomers selected from the group consisting of trimellitic anhydride, pyromellitic dianhydride and polyamide
10 forming polyacids and polyamines.

9. The composition of claim 1 wherein said low molecular weight partially aromatic polyamide is selected from the group consisting of poly(*m*-xylylene adipamide), poly(hexamethylene isophthalamide), poly(hexamethylene adipamide-co-isophthalamide), poly(hexamethylene adipamide-co-terephthalamide), and
15 poly(hexamethylene isophthalamide-co-terephthalamide).

10. The composition of claim 1 wherein said low molecular weight partially aromatic polyamide is poly(*m*-xylylene adipamide) having a number average molecular weight of about 4,000 to about 7,000 and an inherent viscosity of about 0.3 to about 0.6 dL/g.

11. The composition of claim 1 wherein said polyamide comprises at least
20 one low molecular weight aliphatic polyamides selected from poly(hexamethylene adipamide) and poly(caprolactam).

12. The composition of claim 11 wherein said polyamide comprises poly(hexamethylene adipamide) having a number average molecular weight of about
25 3,000 to about 6,000 and an inherent viscosity of 0.4 to 0.9 dL/g.

13. The composition of claim 1 wherein said naphthalenedicarboxylic acid repeat units are derived from a naphthalenedicarboxylic ester and said dicarboxylic acid component further comprises up to about 15 mole percent a second dicarboxylic acid selected from the group consisting of aromatic dicarboxylic acids
30 having 8 to 14 carbon atoms, aliphatic dicarboxylic acids having 4 to 12 carbon

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atoms, cycloaliphatic dicarboxylic acids having 8 to 12 carbon atoms and mixtures thereof.

14. The composition of claim 13 wherein said second dicarboxylic acid is selected from terephthalic acid, phthalic acid, isophthalic acid,
5 cyclohexanedicarboxylic acid, cyclohexanediacetic acid, diphenyl-4,4'-dicarboxylic acid, succinic acid, glutaric acid, adipic acid, azelaic acid, sebacic acid and mixtures thereof.

15. The composition of claim 1 wherein said glycol further comprises at least one additional diol selected from the group consisting of cycloaliphatic diols
10 having 6 to 20 carbon atoms, aliphatic diols having 3 to 20 carbon atoms or mixtures thereof.

16. The composition of claim 15 wherein said additional diol is selected from the group consisting of diethylene glycol, triethylene glycol, 1,4-cyclohexanedimethanol, propane-1,3-diol, butane-1,4-diol, pentane-1,5-diol,
15 hexane-1,6-diol, 3-methylpentanediol-(2,4), 2-methylpentanediol-(1,4), 2,2,4-trimethylpentane-diol-(1,3), 2-ethylhexanediol-(1,3), 2,2-diethylpropane-diol-(1,3), hexanediol-(1,3), 1,4-di-(hydroxyethoxy)-benzene, 2,2-bis-(4-hydroxycyclohexyl)-propane, 2,4-dihydroxy-1,1,3,3-tetramethyl-cyclobutane, 2,2-bis-(3-hydroxyethoxyphenyl)-propane, 2,2-bis-(4-hydroxypropoxyphenyl)-propane and
20 mixtures thereof.

17. A process for forming a blend comprising;
blending

(A) about 80 to about 99 weight % of a base polyester comprising

- 25 (1) a dicarboxylic acid component comprising repeat units from at least about 50 mole naphthalenedicarboxylic acid; and
(2) a diol component comprising repeat units from at least about 50 mole percent ethylene glycol, based on 100 mole percent dicarboxylic acid and 100 mole percent diol; and

B) about 1 to about 20 weight % of a concentrate comprising:

- 30 1) about 1 to about 99 weight % of a carrier resin comprising a

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dicarboxylic acid component comprising repeat units from at least about 60 mole percent naphthalenedicarboxylic acid, and a diol component comprising repeat units from at least about 50 mole percent ethylene glycol, based on 100 mole percent dicarboxylic acid and 100 mole percent diol; and

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- (2) about 1 to about 99 weight% of a polyamide which displays a melting point below the melting point of said carrier resin.

18. The method of claim 17 wherein said polyamide is selected from the group consisting of low molecular weight partially aromatic polyamides having a number average molecular weight of less than 15,000, low molecular weight aliphatic polyamides having a number average molecular weight of less than 7,000 and wholly aromatic polyamides.

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19. The method of claim 17 wherein said polyamide is selected from the group consisting of low molecular weight partially aromatic polyamides having a number average molecular weight of less than 15,000, low molecular weight aliphatic polyamides having a number average molecular weight of less than 7,000.

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 98/04311

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C08L67/02 C08J3/22 //(C08L67/02,77:00)

According to International Patent Classification(IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08L C08J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P, X	WO 97 15629 A (EASTMAN CHEMICAL COMPANY) 1 May 1997 see claims 1-23	1-19
X	"POLY(ETHYLENE NAPHTHALENEDICARBOXYLATE)/POLYAMIDE BLENDS" RESEARCH DISCLOSURE, no. 283, November 1987, page 661/662 XP000026955 see the whole document	1-7, 11-16

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

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"P" document published prior to the international filing date but later than the priority date claimed

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"&" document member of the same patent family

Date of the actual completion of the international search

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 98/04311

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	"POLY(ETHYLENE NAPHTHALENEDICARBOXYLATE)/POLYAMIDE BLENDS" RESEARCH DISCLOSURE, no. 294, 1 October 1988, pages 780-784, XP000112386 see the whole document ---	1, 2, 10, 13-16
A	US 5 340 884 A (MILLS ET AL.) 23 August 1994 cited in the application see claims 1-10 -----	1, 17-19

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 98/04311

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9715629 A	01-05-1997	US 5650469 A	22-07-1997
		AU 7462696 A	15-05-1997
US 5340884 A	23-08-1994	US 5258233 A	02-11-1993
		EP 0633911 A	18-01-1995
		JP 7509011 T	05-10-1995
		MX 9301895 A	01-10-1993
		WO 9320147 A	14-10-1993